

AMENDMENTS TO THE SPECIFICATIONS:

Please amend the paragraph beginning at page 2, line 18, as follows:

The US Bureau of Mines performed extensive additional investigations [1,5-8] to improve the Kroll and Hunter processes. Many other processes have been investigated that include plasma techniques [9-13], molten chloride salt electrolytic processes [14], molten fluoride methods [15], the Goldschmidt approach [16], and alkali metal-calcium techniques [17]. Other processes investigated without measurable success have included aluminum, magnesium, carbothermic and carbo-nitrothermic reduction of TiO_2 and plasma reduction of TiCl_4 [18] ~~without measurable success~~. Direct reduction of TiO_2 or TiCl_4 using mechanochemical processing of ball milling with appropriate reductants of Mg or calcium hydride (CaH_2) also have been investigated [19] without measurable success. Kroll, who is considered as the father of the titanium industry [20] predicted that titanium will be made competitively by fusion electrolysis but to date, this has not been realized.

Please amend the paragraph beginning at page 3, line 6, as follows:

An electrolytic process has been reported [21] that utilizes TiO_2 as a cathode and carbon or graphite as the anode in a calcium chloride electrolyte operated at 900°C . By this process, calcium is deposited on the TiO_2 cathode, which reduces the TiO_2 to titanium and calcium oxide. However, this process is limited by diffusion of calcium into the TiO_2 cathode and the build-up of calcium oxide in the cell, which limits operating time to remove the calcium oxide or replacement of the electrolyte. Also the TiO_2 cathode is not fully reduced which leaves contamination of TiO_2 or reduced oxides such as TiO , mixed oxides such as calcium titanate as well as titanium carbide being formed on the surface of the cathode thus also contaminating

the titanium. Thus, current TiO_2 cathode electrolytic processes are no more commercially viable than ~~[[the]]~~earlier electrolytic processes ~~before it~~.

Please amend the paragraph beginning at page 5, line 17, as follows:

Heretofore the electrolysis of titanium oxide (TiO_2) has not been successful because TiO_2 has little to no solubility in molten salt electrolytes which is also true of other titanium compounds. Titanium tetrachloride (TiCl_4) is a covalent compound that has limited solubility in fused salts and does not readily form complexes with other inorganic salts. It also is highly volatile and is quickly lost from most fused salts. However, since titanium is multivalent, it has been shown that TiCl_4 could be reduced to lower valent ionic species of Ti^{+3} and Ti^{+2} , which do ~~[[show]]~~exhibit some solubility in some molten salts. However, because of secondary reversibility reactions, which lead to loss in current efficiency and poor quality of metal, heretofore no practical process has evolved for electrowinning titanium from a TiCl_4 feed. Investigations of separating the anolyte and catholyte to avoid alternating oxidation and reduction with low current efficiency have not proven successful on a commercial scale.

Please amend the paragraph beginning at page 8, line 19, as follows:

Heretofore, there has not been an electrochemical system to produce titanium similar to electrowinning aluminum in which alumina (Al_2O_3) is soluble in molten cryolite (NaAlF_4) which under electrolysis produces aluminum metal with CO_2/CO being given off at a carbon anode, because there has not been identified a molten salt composition that will dissolve TiO_2 . There is no known molten salt compound or combination of compounds that will dissolve TiO_2 . However, there are molten salt compositions that will dissolve the reduced ~~[[the]]~~ suboxide TiO which is an ionic compound that is very electrically conductive. For example TiO is soluble in molten calcium chloride mixed alkali and alkaline earth chlorides as well as

fluorides or mixed chlorides and fluorides. Thus TiO can be dissolved in CaCl_2 or other salt mixture, and using a carbon/graphite anode electrolyzed to produce titanium at the cathode and CO_2/CO at the anode or oxygen using an inert anode. Since titanium is sensitive to oxygen a separator or diaphragm should be used between the anode and cathode.

Please amend the paragraph beginning at page 9, line 8, as follows:

It is well ~~[[know]]~~known that the higher the temperature of a solvent the greater the solubility of the solute. In this case the higher the molten salt temperature the greater the solubility of a titanium suboxide such as TiO or Ti_2O_3 . In the previous discussions the operating salt temperatures are below that of the melting point of titanium and thus titanium is deposited as a solid in a particulate morphology. As in the case of electrowinning aluminum in which aluminum oxide is soluble in cryolite at over 900°C , the aluminum is in a molten state and thus more easily separated from the molten salt/cryolite. In order to achieve the same advantage with titanium, the molten salt operating temperature should be above the melting point of titanium or about 1670°C . Molten salts that have high melting temperatures that will not readily vaporize at 1670°C or slightly above include calcium fluoride (CaF_2) 1360°C , and barium fluoride BaF_2 1280°C . It was found the titanium suboxides and particularly TiO is quite soluble in CaF_2 at temperatures above 1670°C . Thus titanium is readily electrowon from its suboxides dissolved in CaF_2 or other salts above 1670°C using a carbon/graphite anode that produces CO and CO_2 on electrolysis or an oxygen stable anode that produces oxygen on electrolysis. The titanium produced above 1670°C is in a molten state and thus readily separatable from the molten salt whose density is less than 3.0 g/cc at the operating temperature and titanium is approximately 4.0 g/cc at the operating temperature thus causing the titanium to sink for easy separation.

Please amend the paragraph beginning at page 10, line 14, as follows:

Referring to Figs. [[2 and]] 2a and 2b, the titanium oxide/carbon composite electrode 20 made as above described is employed as an anode in an electrochemical cell 22 with a conventional metallic, e.g., steel electrode 24, and an alkali metal molten salt electrolyte 26.

Please amend the paragraph beginning at page 12, line 18, as follows:

The morphology and size of the titanium deposit is also influenced by the current density of the cathode. The higher the current density the smaller the particle size. Typical cathode current densities are in the 0.05 to 5 amperes/cm² range. The [[most]]more desirable cathode current densities are in the 0.1 to 2.0 amperes/cm² range, and the preferred cathode current densities are in the 0.25 to 1 amperes/cm² range, depending on the morphology of the titanium desired at the cathode. It also has been found that very high current densities can be used at the cathode under high mass flow of the electrolyte and the use of the composite anode. By moving the electrolyte over the cathode surface via gas bubbling or pumping at a fast rate it is possible to electrolytically produce titanium particulate up to cathode current densities of 125 amps/cm².

Please amend the paragraph beginning at page 13, line 13, as follows:

A bench scale electrolytic cell for producing titanium in accordance with the present invention is illustrated in Fig. 3. The cell 30 comprises a cylindrically shaped steel walled vessel 32 having a funnel-shaped bottom closed by a valve 36. The vessel walls 32 are wrapped in a resistance heater (not shown) which in turn is covered by thermal insulation 40. A porous basket 42 formed of carbon fiber mesh is suspended within container 30 and is connected via an anode connector 44 to the plus side of the DC current source. Wall 32 of the steel vessel is connected via a conductor 46 to the negative side of a DC current source. Basket

42 is loaded with pellets or discs 48 of titanium suboxide - carbon flake anode material made as above described. The cell is filled with a molten salt electrode (60:LiCl - 40KCl), the cell is sealed with a top 50, swept with argon purge to remove air, and a voltage of $[[3]]3.0V$ applied which resulted in precipitation of dendritic titanium sponge particles. The titanium sponge particles were then removed via valve 36, separated from the electrolyte, and found to have a purity of 99.9%.

Please amend the paragraph beginning at page 14, line 10, as follows:

From a practical commercial standpoint of producing titanium particulate in which the particulate can be used directly in powdered metallurgical fabrication or consolidated into billets for subsequent rolling into sheet, forging, etc. it is desirable to produce the particulate at as low a cost as possible. High mass transfer and high current density that produces particle sizes that are desirable for commercial applications can be achieved in a cell configuration such as shown in Figure 4.

Please amend the paragraph beginning at page 21, line 19, as follows:

Example 14

An identical system as in Example 13 was created before and $TiCl_2$ was generated, and in trial one, the electrolysis was performed at 40 amps/cm^2 . The titanium particulate produced was in a size range of 20 to 100 microns. In trial two, electrolysis was performed at 125 amps/cm^2 which produced titanium particles in approximately the same size as the 40 amps/cm^2 current density trial. In trial three electrolysis was also performed at 125 amps/cm^2 with argon gas bubbling over the cathode to create a large mass flow. The titanium particulate produced in the high mass flow at 125 amps/cm^2 was in the size range of 40 to 200 microns. The titanium suboxide-carbon composite anode provides the opportunity to operate at very high cathode

current densities and in a high mass flow regime.

Please amend the paragraph beginning at page 22, line 6, as follows:

Example 15

TiO₂ and carbon were heated under a pressure of 0.01 residual argon atmosphere to 1850°C which produced TiO and CO. The TiO was mixed with stoichiometric carbon and a binder and molded into a block which was heated to 1100°C which formed a composite anode. The resulting composite anode was placed in a salt mixture of 60NaCl-40MgCl₂ and 20 mole percent NaF based on the chloride salt mixture operated at 600°C. In trial one, the electrolysis was performed at 0.15 amps/cm² and titanium particulate in the size range of 50 to 300 microns was produced. In trial two, a titanium sponge was placed in a small crucible immersed in the salt bath and TiCl₄ was bubbled onto the sponge that produced TiCl₂ until the concentration was 8% TiCl₂ in the salt. Electrolysis was performed at 0.15 amps/cm² which produced titanium particulate in the 200 to 500 micron size. The oxygen content was 380 parts per million.

Please amend the paragraph beginning at page 25, line 9, as follows:

Example 22

The molten salt bath electrolyte of CaCl₂ operated at 900°C showed a considerable solubility of the reduced suboxide of titanium TiO. In a salt bath operated at 900°C 5 wt % TiO was added and electrolysis conducted with a carbon anode. Titanium particulate was deposited on the cathode at a current density of 1 amp/cm². In a second trial, a porous alumina diaphragm was used around the anode to prevent any oxygen from diffusing to the deposited titanium on the cathode and contaminating the deposited titanium particulate.